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<p>(54) Title: POWDER SLURRY COMPOSITION CONTAINING PARTICULATE CARBAMATE FUNCTIONAL COMPOUNDS</p>			
<p>(57) Abstract</p>			
<p>The invention provides a powder slurry composition having a particulate component (a) dispersed in a liquid component (b). Component (a) comprises a solid or particulate compound (i) comprising the reaction product of a polyisocyanate (A) and a compound (B). Polyisocyanate (A) is of the formula $[R(NCO)_y]_x$, where $x = 1$ or higher, $y = 2$ or higher, and R has C_n symmetry when $n = 2$ or higher. Compound (B) comprises both an isocyanate-reactive group and a functional group selected from the group consisting of a carbamate group and groups convertible to a carbamate group after reaction of compound (B) with polyisocyanate (A). One or both of component (a) and (b) comprise a crosslinking agent (ii) reactive with particulate compound (i).</p>			

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**POWDER SLURRY COMPOSITION CONTAINING
PARTICULATE CARBAMATE FUNCTIONAL COMPOUNDS.**

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Field of the Invention

The present invention relates to powder slurry compositions containing particulate, solid carbamate functional compounds. The invention provides a powder slurry composition comprising a particulate component (a) dispersed in a liquid component (b).

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Background of the Invention

Powder slurry compositions have been used to provide a variety of advantages in the coating of articles. Powder slurry compositions typically include a first component that is in solid particulate form and a second component that is liquid. The first component is dispersed in the second component to provide a slurry which can be applied using conventional spray application equipment and techniques.

Aqueous powder slurry compositions provide the advantages of powder coating compositions with the ease of application of traditional solvent borne coatings. As a result, powder slurry compositions have the potential for environmental and/or financial advantages.

However, powder slurry compositions may present manufacturing, performance and/or application challenges.

Traditional powder slurry compositions often utilize epoxy acid compound systems. Such systems can sacrifice scratch and mar resistance in order to obtain

acceptable water resistance, chip resistance and etch resistance.

The nature of the powder coating composition used in the powder slurry composition requires the use of initial temperatures above the T_g of the powder resin, followed by temperatures sufficient to affect crosslinking. Thus, high cure 5 schedules are often required. It will be appreciated that application concerns and energy costs encourage the use of powder slurry compositions having lower T_g resins. The use of lower T_g resins facilitates more rapid flow, improved appearance and lower cure temperatures.

However, storage and manufacturing problems can result when powder 10 slurry compositions having lower T_g resins are utilized. Manufacturing is particularly challenging, especially with acid epoxy compound systems. Separation, precipitation and/or agglomeration of the solid particulate component during storage may also be observed.

Inferior film adhesion and/or cracking of the applied powder slurry film 15 during curing are sometimes observed, particularly when the powder slurry is applied over a previously applied coating. These negative performance characteristics can be magnified by higher film builds and storage stability.

Finally, finished films obtained from powder slurry compositions can 20 exhibit variable gloss and/or inferior performance characteristics, particularly when balancing scratch and mar resistance against water resistance, chip resistance and etch resistance. It is often difficult to achieve an acceptable balance of properties among these characteristics, especially with traditional acid epoxy powder/powder slurry compound systems.

Thus, it is desirable to provide improved powder slurry compositions wherein the foregoing disadvantages are either eliminated or are minimized. Prior art attempts hereto have been unsuccessful.

It is expected that the use of one or more particulate carbamate functional 5 resins will provide powder slurry compositions having an advantageous balance of properties.

Summary of the Invention

The invention provides a powder slurry composition having a particulate component (a) dispersed in a liquid component (b). Component (a) comprises a 10 solid or particulate compound (i) comprising the reaction product of a polyisocyanate (A) and a compound (B). Polyisocyanate (A) is of the formula $[R(NCO)_y]_x$, where $x = 1$ or higher, $y = 2$ or higher, and R has C_n symmetry when $n = 2$ or higher. Compound (B) comprises both an isocyanate-reactive group and a functional group selected from the group consisting of a carbamate group and 15 groups convertible to a carbamate group after reaction of compound (B) with polyisocyanate (A). One or both of component (a) and component (b) will comprise at least one crosslinking compound (ii).

Detailed Description of the Invention

The powder slurry composition of the invention requires two components, 20 a first component (a) in solid or particulate form that is dispersed in a liquid component (b).

First component (a) comprises a particulate compound (i) comprising the reaction product of a polyisocyanate (A) and a compound (B). Polyisocyanate (A)

has a $T_g \leq 30^\circ\text{C}$ and is of the formula $[\text{R}(\text{NCO})_y]_x$, where $x = 1$ or higher, $y = 2$ or higher, and R has C_n symmetry when $n = 2$ or higher.

The compound (i) of the invention is particularly suitable for use in powder slurry coating compositions. While not wishing to be bound to a particular theory, the particular advantages of compound (i) are believed to be due in part to polyisocyanate (A).

Polyisocyanate (A) is of the formula $[\text{R}(\text{NCO})_y]_x$, where $x = 1$ or higher, $y = 2$ or higher, and R has C_n symmetry wherein $n = 2$ or higher. Thus, isocyanate (A) is monomeric when $x = 1$, a uretdione or polyisocyanate dimer if $x = 2$, an isocyanaurate when $x = 3$, or a polymeric homopolymer if x is greater than 3. x may be 1 or higher but is preferably 1, 2, or 3, more preferably $x = 1$ or 3, and most preferably, $x = 3$. y may be 2 or higher but is preferably, 2, 3, or 4 and is most preferably 2.

As indicated above, R must have a particular symmetry in order to provide a polyisocyanate (A) suitable for use in the instant invention. As used herein, a molecule with symmetry means that certain parts of the molecule can be interchanged, via a symmetry operation, with others without altering either the identity or the orientation of the molecule..

Symmetry operations are geometrically defined ways of exchanging equivalent parts of a molecule. However, such operations are symmetry operations if, and only if, the appearance of the molecule is exactly the same relative to the pre- and post- symmetry operation view. Thus, the term "symmetrical" as used herein refers to a molecular having an appearance that

appears identical relative to the pre- and post- symmetry operation views. Put another way, “[a] molecule possesses a symmetry element if the application of the operation generated by the element leaves the molecule in an indistinguishable state.” *Molecular Symmetry and Group Theory*, Alan Vincent, Wiley & Sons,

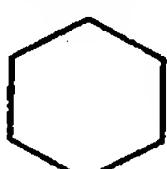
5 NY, 1977, reprinted 1981, page 21, hereby incorporated by reference

The instant application is concerned only with proper rotation symmetry operations. Proper rotation, also referred to as “ C_n ”, refers to simple rotation about an axis passing through the molecule by an angle $2\pi/n$ or an angle $360^\circ/n$.

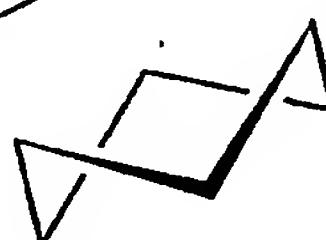
A molecule is said to have a C_n symmetry element if after undergoing a proper 10 rotation C_n operation, it’s appearance is indistinguishable from it’s appearance prior to undergoing the proper rotation C_n operation, irrespective of conformational isomers. Put another way, a molecule possesses a symmetry element, in this case C_n , when one or more of its conformational isomers possesses that symmetry element. The highest symmetry element that belongs to 15 any conformational isomer of the molecule is assigned to the molecule.

While it may be appreciated that all molecules have C_n symmetry where n is 1, the instant application is only concerned with R groups also having C_n symmetry where n is 2 or higher.

For example, the two most common conformational isomers of 20 cyclohexane



are the chair:

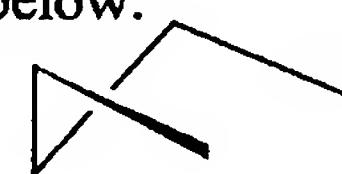


which has a C_3 proper rotation axis, and the boat conformation:



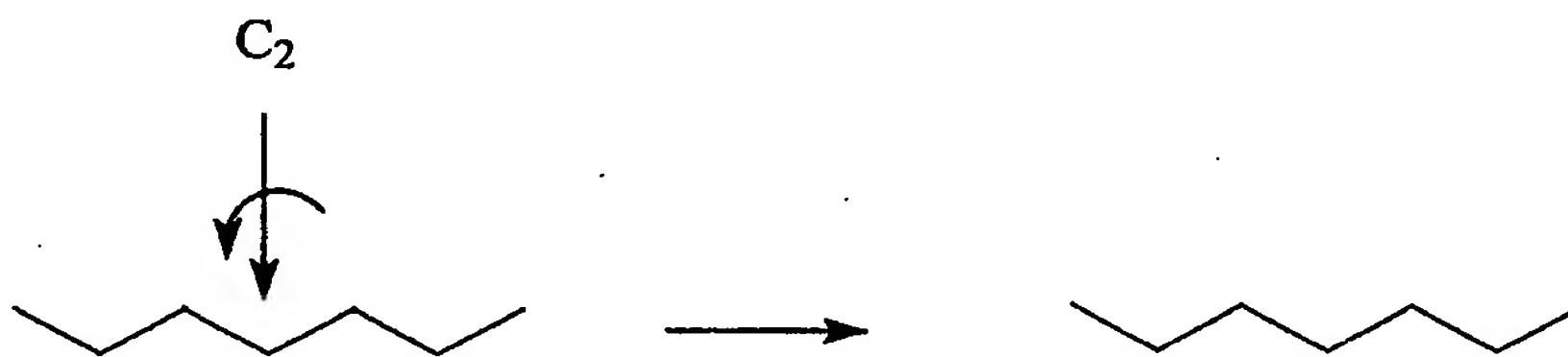
which has a C_2 proper rotation axis. As a result, cyclohexane may be defined as having a molecular C_3 proper rotation axis (C_n wherein $n = 3$) without having to define its conformation.

Similarly, hexane, with the freedom of motion around its numerous single
5 bounds can exist in a large number of configurations such as the one below:



One of the conformational isomers of hexane (shown below) possess a C_2 proper rotation axis. Therefor, hexane may be said to possess a C_2 (wherein $n = 2$) molecular symmetry element.

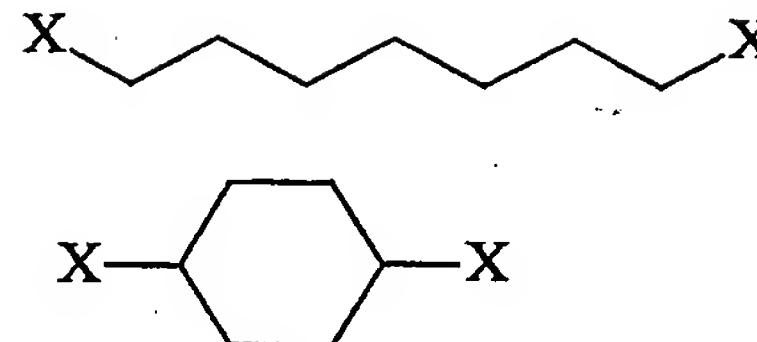
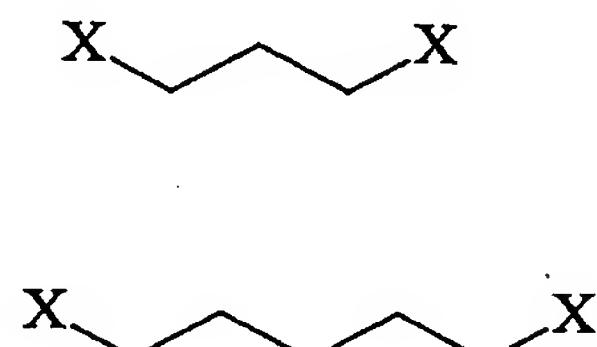
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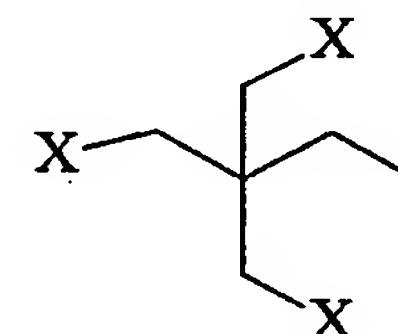
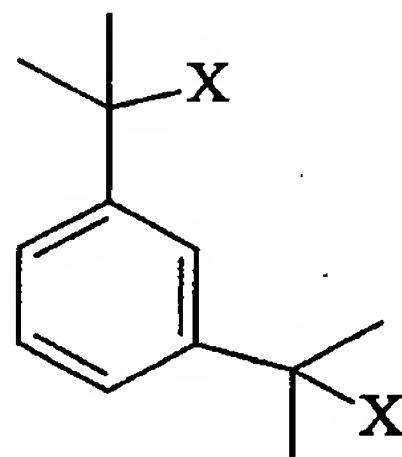
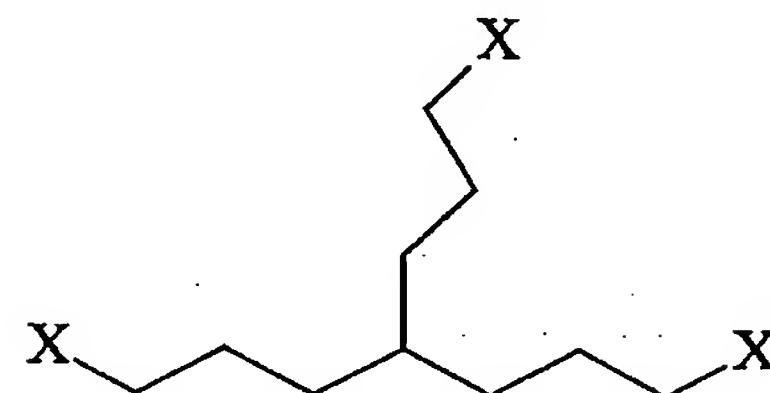
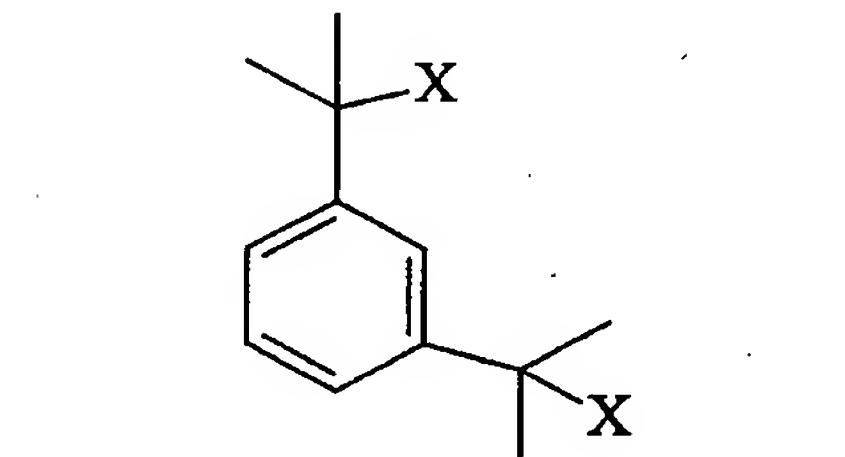
R is an alkyl or cycloalkyl group having at least four carbons and a
15 particular symmetry as herein described. Preferably, R will be an alkyl group having from four to 12 carbons and most preferably R will be an alkyl group having from four to 8 carbons. R will preferably be an alkyl group of the formula C_nH_{2n} . Examples of illustrative R groups include C_4H_8 and C_6H_{12} . A particularly preferred group is C_6H_{12} . Illustrative examples of suitable R groups

include alkyl groups such as:

5



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where "X" marks the location of an isocyanate group.

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Examples of polyisocyanates suitable for use as polyisocyanate (A)

include 1,6-hexane diisocyanate, *m*-tetramethyl xylene diisocyanate,

dicyclohexylmethane-4,4'-diisocyanate, 1,4-butane diisocyanate, 1-isocyanato-

2,2'(bis(isocyanatomethyl)propane, 1,7-diisocyanato-4-(3-

isocyanatopropyl)heptane, the respective dimers thereof, the respective trimers

20 thereof, and mixtures thereof. Preferred polyisocyanates (A) are 1-isocyanato-

2,2'(bis(isocyanatomethyl)propane, 1,6-hexane diisocyanate, *m*-tetramethyl

xylylene diisocyanate and the respective dimers thereof, the respective trimers

thereof, and mixtures thereof. Most preferred as polyisocyanate (A) is 1,6-hexane diisocyananate, the respective dimers thereof, the respective trimers thereof.

Compound (B) is a compound containing an isocyanate-reactive group and either a carbamate group or a group convertible or capable of converting to a carbamate group after reaction of compound (B) with polyisocyanate (A) is completed. Compound (B) is preferably a compound containing an isocyanate-reactive group and a carbamate group.

Compounds containing an isocyanate-reactive group and a carbamate group are preferably hydroxyalkyl carbamates such as hydroxypropyl carbamate or hydroxybutyl carbamate, or aminoalkyl carbamate groups such as aminoethyl carbamate, aminopropyl carbamate and the like.

Compounds containing an isocyanate-reactive group and a group convertible or capable of converting to a carbamate group after reaction of compound (B) with polyisocyanate (A) is completed, include hydroxy-containing cyclic carbonate compounds convertible to carbamate by reaction with ammonia (e.g., the reaction product of glycidol and CO₂), monoglycidyl ethers (e.g., glycidyl propyl ether convertible to carbamate by reaction with CO₂ and then ammonia), allyl alcohols where the alcohol group is reactive with NCO and the double bond can be converted to carbamate by reaction with peroxide, and vinyl esters where the ester group is reactive with NCO and the vinyl group can be converted to carbamate with reaction with peroxide, then CO₂, and then ammonia.

Also suitable as compound (B) are compounds having a carbamate group as well as a group that can be converted into a carbamate. The carbamate group

can then react with the isocyanate group to form an allophanate. The carbamate-convertible group can then be converted into a carbamate. An example of such a compound is allyl carbamate.

Preferably, compound (B) will be a hydroxyalkyl carbamate compound
5 having an alkyl group of from 2 to 6 carbons, especially from 2 to 4 carbons.

Most preferably, (B) will be hydroxylpropyl carbamate.

The compound (i) of the invention will preferably have a molecular weight
of from 350 to 1900 and most preferably from 460 to 900. The equivalent weight
per carbamate functional group can range from 175 to 450 and preferably from
10 175 to 350.

Compound (i) will typically have no acid or hydroxy groups.

Compound (i) is normally a solid at 25°C, the term "solid" referring to a
substance of definite shape and relatively great density, low internal enthalpy, and
great cohesion of its molecules. *Grant & Hackh's Chemical Dictionary, Fifth*
15 *Edition McGraw-Hill, Inc. pg.541.* Compound (i) will typically have a $T_g \geq$
30°C.

The compound (i) of the invention will typically be processed in one or
more solid masses, for example sheets, rolls, or drops, by accepted powder
compound manufacturing techniques. After solidifying, the mass is broken into
20 particles having a desired size and shape. The size and shape of the compound
particles is dependent upon handling, processing, and equipment considerations.

Preferably, the compound (i) will be in the shape of flat chips or discs
having regular or irregular dimensions. Particles having an average particle size

of from 1 to 3 inches are preferred, with average particle sizes of from 1 micron to up to 1 inch most preferred. Particle size as used herein refers to the average diameter of an object having irregular boundaries that can be determined with known test methods.

5 It will be appreciated that particulate component (a) is preferably a powder coating comprising compound (i).

Prior to dispersion in liquid component (b), component (a) should have an average particle size of from 0.1 to 100 microns. A preferred average particle size range for component (a) at this time, is from 3 to 60 micron. A 30 to 45 micron 10 average particle size is most preferred. Traditional extrusion and grinding processes may be used to obtain particulate component (a) within these ranges.

Compound (i) may initially have an average particle size within or outside this range resulting from known powder compound manufacturing techniques.

Solid particulate first component (a) upon admixture with liquid 15 component (b) will typically be subsequently treated so as to reduce the above particle sizes to those more desirable for a powder slurry composition. Once in combination with component (b), the powder slurry composition may be subjected to a particle size reduction treatment such as wet milling, microfluidization, cavitation, or other high sheer, low temperature techniques known to those skilled 20 in the art. Thus the particle size of the powder slurry composition of the invention after a particle size reduction treatment is typically from 0.1 to 20 microns, more preferably from 0.1 to 15 microns and most preferably, will have an average particle size of from 0.1 to 12 microns.

Component (a) may be obtained according to conventional techniques and methods. The compositions of the invention are advantageous because compound (i) permits the use of higher processing temperatures. Moreover, during the preparation of solid particulate component (a), or subsequent thereto, pigments, 5 pigment dispersions, modifiers, dispersion aids, regulators, flow modifiers, fillers, and/or additives may optionally be added as desired.

Liquid component (b) may be one or more liquids or solvents suitable for the dispersment of particulate compound (a). Examples of suitable liquids or solvents include water, water soluble solvents, and organic solvents and mixtures 10 thereof. Illustrative water-soluble solvents are alcohols. Examples of illustrative water soluble solvents and/or organic solvents are ethyleneglycol monomethylether, ethyleneglycol monoethylether, ethyleneglycol monobutylether, methanol, ethanol, isopropanol, n-butanol, sec-butanol, tert-butanol, dimethylformamide, etc. Preferred liquids for use in are water, alcohols 15 and mixtures thereof. A most preferred liquid component (b) is water. Such solvents will typically be used in quantities of from 0 to 10, based on total weight of the powder slurry, and preferably from 0 to 1.0%.

The weight proportion of component (a) and component (b) is usually from 90:10 to 50:50, preferably from 75:25 to 60:40, in terms of solid component. 20 The powder slurry composition of the invention may further comprise additional optional components such as one or more solvents or additives such as pigments, fillers, catalysts, corrosion inhibitors, modifiers, dispersants, flow

additives, and mixtures thereof. These materials may be incorporated into component (a), component (b) or the mixture thereof.

For the preparation of the powder slurry composition of the invention, the required and optional components may be combined in an optional order and 5 mixed well by conventional processes. Component (b) may be mixed with component (a) and a pigment and, if necessary, further with other optional components. Alternatively, pigment may be mixed with component (b) to form a pigment paste, which is then admixed with a mixture of component (a) and component (b). A grinding or milling operation may follow such admixture. A 10 preferred method of manufacture is disclosed in U.S Patent 5,379,947, hereby incorporated by reference. The powder slurry composition of the invention has advantageously low VOCs as a result of the unexpected benefits of the components of the invention.

The powder slurry composition of the invention can be applied by spray or 15 by electrostatic deposition and are useful as both basecoat and topcoat applications. It is expected that the resultant coating compositions form smooth films with advantageous performance properties.

One or both of component (a) and component (b) will comprise a crosslinking agent (ii) reactive with particulate compound (i).

20 Crosslinking agent (ii) may be in liquid or solid form at the time of incorporation into component (a), component (b) or the mixture thereof. The use of crosslinking agent (ii) in liquid form and incorporated into liquid component (b) is most preferred.

Illustrative examples of crosslinking agent (ii) include one or more compounds having a plurality of functional groups that are reactive with compound (a). Suitable reactive groups include active methylol or methylalkoxy groups on aminoplast crosslinking agents or on other compounds such as 5 phenol/formaldehyde adducts, acrylamide groups, isocyanate groups, siloxane groups, cyclic carbonate groups, and anhydride groups.

Examples of the at least one crosslinking compound (ii) include melamine formaldehyde compound (including monomeric or polymeric melamine compound and partially or fully alkylated melamine resin), urea resins (e.g., 10 methylol ureas such as urea formaldehyde resin, alkoxy ureas such as butylated urea formaldehyde resin), polymers having acrylamide groups, polymers having methylol or alkoxyethyl groups, polyanhydrides (e.g., polysuccinic anhydride), and polysiloxanes (e.g., trimethoxy siloxane). Monomeric and/or low oligomeric aminoplast resins such as melamine formaldehyde resins or urea formaldehyde 15 resins are especially preferred.

The ratio of equivalents of compound (a) to equivalents of crosslinking agent (ii) is about from 0.5:1.0 (a:b) to 1.5:1.0, preferably from about 0.8:1.0 to 1.2:1.0.

The powder slurry compositions of the invention can be applied by spray 20 or by electrostatic deposition and are useful as both basecoat and topcoat applications. It is expected that the resultant coating compositions form films having an acceptable appearance with advantageous performance properties.

The powder slurry compositions of the invention may be applied to a variety of substrates for use in various end use applications such as automotive, furniture, industrial, lawn and garden, appliances, electrical equipment, and the like.

5 Suitable substrates include metal, plastic, wood, ceramics, composites and mixtures thereof. Metal and/or plastic substrates are preferred. Substrates will preferably be clean prior to application of the powder coating. Substrates may be optionally pretreated with phosphating, chromatizing and similar pretreatment methods to improve adhesion and/or appearance. It will be appreciated that
10 pretreatment selection is dependent upon the desired substrate and end use application.

After application, the coated part is subjected to a cure schedule sufficient to effect flow and cure. As used herein, "cure schedule" refers to the time/temperature relationship required to effect complete curing of a
15 thermosetting powder coating. Typical cure schedules for the powder coatings of the invention involve part temperatures of from 250 to 400°F and time at part temperature of from 10 to 30 minutes. Preferred cure schedules are from 250 to 400 °F and time at part temperature of from 10 to 20 minutes.

The inventions are further described in the following nonlimiting
20 examples.

Example 1Preparation of compound according to the invention.

A mixture of 139.9 parts of hydroxy propyl carbamate, 98.8 parts of 1,6-hexanediisocyanate (HDI), 10.5 parts of toluene and 0.8 parts of tin octoate were 5 mixed and heated until an exothermic reaction occurred. The maximum temperature for the reaction mixture was kept below 100° C. 28.5 parts of butyl acetate was added to the resulting solid resin. The mixture was heated until the system was liquid (132°C). When cooled to room temperature, approximately 25°C, a solid compound was obtained.

10

Example 2Prophetic preparation of a powder slurry composition according to the invention.

Three hundred grams of the compound made in example #1 is ground in an ACM mill to an average particle size of 25 – 35 microns and set aside. One gram of Abex EP-110¹, is added to 100 grams of Cymel 303² and mixed for 5 15 minutes with a standard mixing blade. A stainless steel vessel with a cowles mixing blade is loaded with 200 grams of water. Keeping the speed low the following items are added in order: 5 grams of Disperse AYD W-22,³ 0.1 grams of Triton X100⁴, 2.5 grams of propylene glycol, and 3 grams of Acrysol RM-8W⁵. The mixer speed is increased to 4 – 500 rpm for 5 minutes prior to the addition of

¹ a surfactant, commercially available from Rhodia.

² a hexamethoxymethyl melamine, commercially available from Cytec.

³ a dispersant, commercially available from Daniel Products.

⁴ a nonionic surfactant, commercially available from Union Carbide.

⁵ a thickening agent, commercially available from Rhom & Haas.

132.5 grams of the ground resin. The vessel is allowed to mix for 10 minutes. Next 43 grams of the Cymel 303 premixed above is added followed by 7 grams of Nacure 5225⁶ and 110 grams of water. The vessel is mixed for 10 minutes after which the cowles blade is replaced by a media disk mixing blade. Enough small 5 (1.1 – 1.4 mm) ceramic media is added to the vessel to equal 50% of the volume of the mixture. The temperature of the mixture is maintained at 18 – 23°C, and is stirred at 1200 rpm. The particle size is monitored over time to attain a final median particle size of 4 – 5 microns. The disk is removed and the media filtered out using a 55 micron nylon filter. The viscosity is adjusted to 35 – 45" #4 Ford 10 cup with water. The slurry is sprayed out of a standard siphon spraygun over a heat flashed but not cured waterborne base coat, allowed to flash 5 minutes at room temperature and then baked for 20 – 30 minutes at 270°F.

⁶ a sulfonic acid catalyst, commercially available from King Industries.

We claim:

1. A powder slurry coating composition comprising

(a) a particulate component comprising

(i) a particulate compound comprising the reaction product of a

5 polyisocyanate (A) and a compound (B),

dispersed in

(b) a liquid component, wherein

compound (B) comprises an isocyanate-reactive group and a functional

group selected from the group consisting of a carbamate group and groups

10 convertible to a carbamate group after reaction of compound (B) with

polyisocyanate (A) and

polyisocyanate (A) has a $T_g \geq 30^\circ\text{C}$ and is of the formula $[\text{R}(\text{NCO})_y]_x$,

where $x = 1$ or higher, $y = 2$ or higher, and R has C_n symmetry wherein $n = 2$ or

higher.

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2. The powder slurry coating composition of claim 1 wherein R has a

molecular weight between 50 and 165.

3. The powder slurry coating composition of claim 1 wherein x is 1, 2, or 3

20 and y is 2 or 3.

4. The powder slurry coating composition of claim 1 wherein n is 2.

5. The powder slurry coating composition of claim 1 wherein the polyisocyanate (A) is a monomeric diisocyanate.

6. The powder slurry coating composition of claim 1 wherein the polyisocyanate (A) is an isocyanurate.

5

7. The powder slurry coating composition of claim 1 wherein the polyisocyanate (A) is selected from the group consisting of 1,6-hexane diisocyanate, *m*-tetramethyl xylene diisocyanate, dicyclohexylmethane-4,4'-diisocyanate, 1, 4-butane diisocyanate, 1-isocyanato-

10 2,2'(bisiscyanatomethyl)propane, the respective dimers thereof, the respective trimers thereof, and mixtures thereof.

8. The powder slurry coating composition of claim 1 wherein compound (B) is a hydroxyalkyl carbamate.

15

9. The powder slurry coating composition of claim 8 wherein compound (B) is hydroxy propyl carbamate.

10. The powder slurry coating composition of claim 1 wherein one or both of 20 component (a) and component (b) comprise at least one crosslinking agent (ii) which is reactive with particulate compound (i).

11. The powder slurry coating composition of claim 1 wherein crosslinking agent (ii) is one or more aminoplast resins.
12. The powder slurry coating composition of claim 1 further comprising one or more members selected from the group consisting of thickening agents, surfactants, dispersents, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/27518

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08G18/38 C09D175/04 C09D201/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08G C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 661 315 A (BASF CORP) 5 July 1995 (1995-07-05) page 2, line 30 -page 4, line 5 page 5, line 10 - line 29 example 3 ---	1-3, 6, 8-11
A	EP 0 767 187 A (BASF CORP) 9 April 1997 (1997-04-09) page 2, right-hand column, line 16 -page 3, left-hand column, line 8 example 1 ---	1-5, 8-11
A	EP 0 516 066 A (HERBERTS & CO GMBH) 2 December 1992 (1992-12-02) example 4 ----	1

Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

15 August 2000

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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